Short communication

Silver nanoparticles embedded in modified polyallylamine resin as efficient catalysts for alkyne–azide 1,3-dipolar cycloaddition in water

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Xian-Liang Zhao [a,*], Ke-Fang Yang [b,**], Yan Zhang [a], Li-Wen Xu [b], Xiao-Qing Guo [a]

[a] School of Biological and Chemical Engineering/School of Light Industry, Zhejiang University of Science and Technology, Hangzhou 310023, China
[b] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, China

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ABSTRACT

A silver nanoparticle composite based on modified polyallylamine has been synthesized by a simple chemical route and its catalytic activity has been tested for alkyne–azide cycloaddition reaction. This silver nanocomposite shows an excellent catalytic activity at 80 °C for the synthesis of 1,4-disubstituted 1,2,3-triazole by alkyne–azide cycloaddition. The solid silver nanocomposite catalyst was characterized by transmission electron microscopy, Fourier-transform infrared spectroscopy, X-ray diffractometry and thermogravimetric analysis. The developed catalyst is stable in air, easy to prepare and can be recovered easily and reused ten times without a significant decrease in activity.

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1. Introduction

The Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes is a widely studied "click" reaction to synthesize 1,2,3-triazoles [1]. This reaction has been applied extensively in pharmaceuticals, drug discovery, agrochemicals, dyes, corrosion inhibitors, photostabilizers, photographic materials and biochemistry [2–7]. The copper-catalyzed alkyne–azide cycloaddition is regarded as the most efficient click chemistry [8–10]. The heterogeneous nature of catalysts offers advantages of thermal stability and reusability [11–14]. The catalytic activity of copper nanoparticles (Cu NPs) in the azide–alkyne click reaction has received much interest [15–21]. Silver nanoparticles (Ag NPs) have been employed catalysts in organic synthesis, However, Ag NPs have received less attention in terms of their application in the azide–alkyne click reaction [22]. Although Jana et al. reported on a silver–graphene nanocomposite for a "one-pot" azide–alkyne click reaction, the application of other Ag NPs immobilized on polymers still needs to be explored [23].

Polymers are excellent host materials for the preparation of metal nanoparticles. Various synthetic polymers, such as poly(methyl methacrylate), polystyrene, poly(vinyl alcohol) and poly(vinyl pyrrolidone),

have been used in the synthesis of metal nanoparticles [24–28]. However, minimal work has been carried out where polyallylamine has been used as a capping agent to stabilize metal nanoparticles [29–31]. Among them, Kuo just reported the syntheses and characterization of silver nanoparticles stabilized by poly(allylamine) (PAA) and by poly-ethyleneiminated poly-(allylamine). The application of Ag NPs still needs to be explored.

Herein, we describe the advantages of Ag NPs in modified polyallylamine as a simple, inexpensive and general and efficient heterogeneous catalyst for use in the Huisgen 1,3-dipolar reaction of alkyne–azide cycloaddition in water.

2. Experimental

2.1. Instruments

Infrared spectra were recorded on a Perkin Elmer Fourier-transform infrared (FTIR) spectrometer using KBr. FEI Technai G2 transmission electron microscope was used for transmission electron microscopic (TEM) image of sample. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo 851E instrument. X-ray diffraction patterns were recorded on a Rigaku, D-5000 diffractometer, using Ni-filtered Cu-K radiation ($\lambda = 1.5405$ Å). ^{1}H NMR spectra were recorded on a 400 (Varian, Palo Alto, USA) spectrometer in CDCl$_3$ solution with tetramethylsilane as an internal standard. Chemical shift values are given in parts per million.

* Correspondence to: X.-L. Zhao, School of Biological and Chemical Engineering, Zhejiang University of Science and Technology, Hangzhou 310023, China.
** Corresponding author.
E-mail addresses: xlzhao@iccas.ac.cn (X.-L. Zhao), kfyang@hznu.edu.cn (K.-F. Yang).
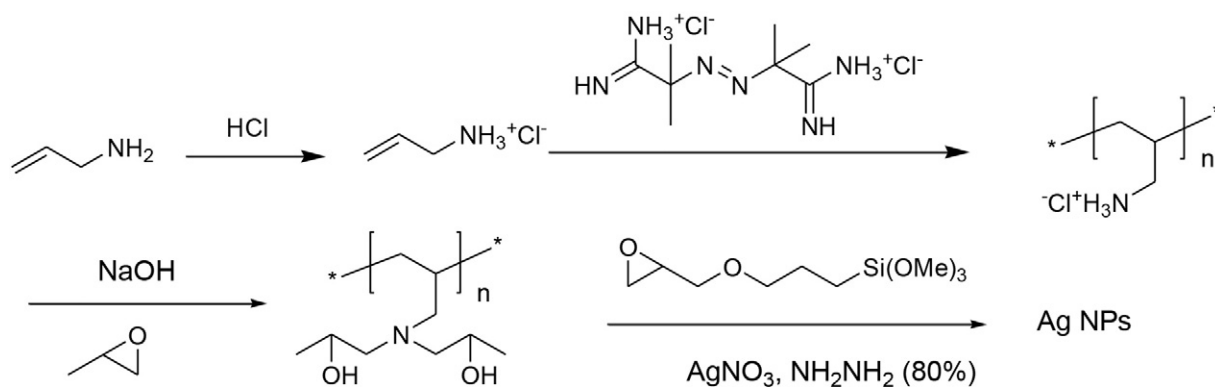
Scheme 1. Synthesis for silver nanocomposite.

2.2. Preparation of silver nanocomposite

The modified polyallylamine (10.0 g) was dissolved in water (30.0 mL) to obtain a clear solution at room temperature. Silver nitrate (3.26 g) was dissolved in water (10.0 mL) and added into the solution at room temperature. Ammonia water was added into the solution to obtain a clear solution at room temperature. (3-Glycidoxypropyl)methyldiethoxysilane (4.0 g) was added into the mixture at room temperature. The mixture was heated to a viscous solid at 120 °C, then cooled to room temperature. Hydrazine hydrate (80 wt.%) (20 mL) was added and stirred at room temperature for 24 h. The resultant brown solid was washed with water and dried at 60 °C for 12 h under vacuum to afford Ag NPs (16.2 g).

2.3. Application of silver nanocomposite as an efficient catalyst in organic reactions

A mixture of benzylazide (133.0 mg, 1.0 mmol), phenylacetylene (102.0 mg, 1.0 mmol), silver nanocomposite (10.0 mg) and water (1.0 mL) was stirred at 80 °C in a test tube. The reaction was extracted using dichloromethane (10.0 mL). The combined organic extract was washed with water (5.0 mL) and dried using anhydrous magnesium sulfate. The solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether, 1:10) to afford a colorless solid **3a** (0.223 g, 95%).
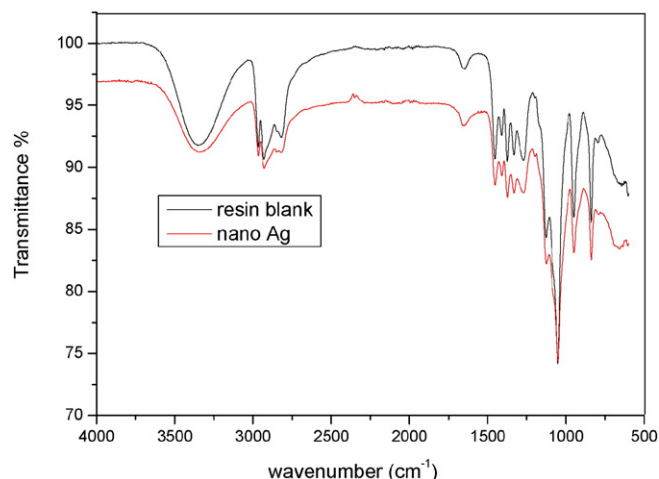
3. Results and discussion

3.1. Preparation of Ag NPs

The synthesis strategy for the silver–polyamine nanocomposite is shown in the Scheme 1. Polyallylamine was synthesized according our previous work [32]. The modified polyallylamine has a strong tendency to form gel in aqueous solution. This gel that contains hydroxy and amino groups protects and stabilizes the Ag NPs in its strong gel mesh and acts as an excellent surface capping agent in the process.

3.2. Catalyst characterization

3.2.1. FTIR spectra of Ag NPs and blank resin

The FTIR spectra of the blank and silver resin are shown in Fig. 1. The O–H absorption band shifted slightly compared with that of blank polymer composite in the FTIR analysis. This indicates that an interaction occurs between these groups and nanosilver.

3.2.2. X-ray diffractometry of Ag NPs and blank resin

Fig. 2a shows the X-ray diffraction pattern of the blank resin. The resin reflection at 2θ of 18.82° corresponds to the amorphous part of the resin. The resin reflection at 2θ of 28.42°, 40.53°, 50.3°, 66.42° and 73.84° corresponds to the crystalline part of the resin [33–34].

Fig. 2b shows the X-ray diffraction pattern of the silver resin. The reflections at 2θ of 38.3°, 43.6°, 64.6° and 77.80° correspond to (111), (200), (220) and (311) planes of silver, respectively [24–28]. The reflection of resin at 2θ of 19.22° corresponds to the amorphous part of the
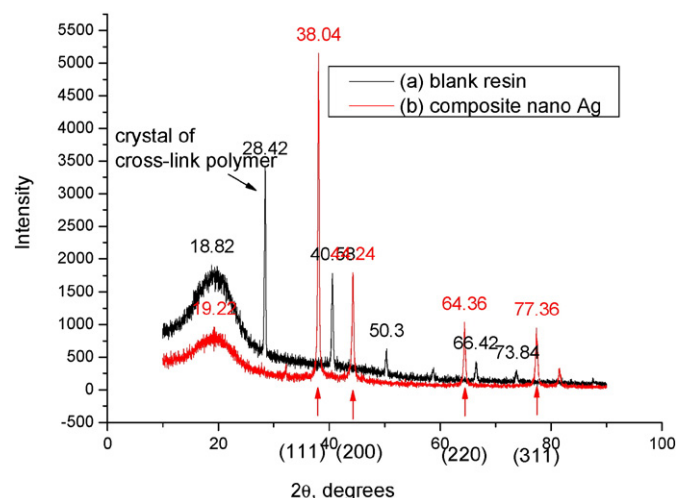

Fig. 1. FTIR spectra of Ag NPs and blank resin.

Fig. 2. X-ray diffraction pattern of Ag NPs and blank resin.

a
The image formed before using as catalyst for 1,

3-dipolar cycloaddition.

b
The image formed before using as catalyst for 1,

3-dipolar cycloaddition at 80 °C.

Fig. 3. TEM image of Ag NPs.

resin. The reflective crystalline part of the resin at 2θ disappeared compared with the reflection of the blank resin. Nanosilver was stabilized by amine and hydroxyl groups on the resin that destroy the crystalline part of the resin.

3.2.3. TEM of Ag NPs and blank resin

Fig. 3a shows an image of the Ag NPs before using the reaction. The TEM image indicates that the Ag NPs are dispersed uniformly in the resin. Fig. 3b shows an image of the Ag NPs after they had been used in the reaction. The TEM image (Fig. 3b) indicates that the Ag NPs were stabilized by the resin. The Ag NPs are still dispersed uniformly in the resin even in hot water. The results also proved that the activity of Ag NPs can be used for reuse.

3.2.4. TGA of Ag NPs and blank resin

TGA of Ag NPs is compared with a blank resin in Fig. 4. The TGA curve of the blank resin and the Ag NPs shows a mass loss (2 wt.%) below 100 °C that corresponds to the loss in physically adsorbed water. In the TGA curve for the blank resin and Ag NPs, two regions exist that correspond to different mass loss ranges. The first region is approximately 250 °C and displays a mass loss that is attributable to the loss of trapped water from the resin. A mass loss of approximately 50 wt.% occurred

between 370 and 450 °C and this is related to the sudden resin mass loss. This result shows that the blank resin and Ag NPs have a greater thermal stability.

3.3. Catalytic studies

We investigated the catalytic activity of Ag NPs in the alkyne–azide cycloaddition in water. To develop an optimal catalytic system, benzyl azide and phenylacetylene were used as model reactants to test the catalytic activities of Ag NPs. The results are summarized in Table 1. Water is considered to be a benign environmental solvent, and was therefore used as solvent to test the effect of temperature. As the temperature rose from 50–80 °C, the triazole yield increased from 24% to 92% in

Table 1
Temperature effects on the reaction of benzylazide with phenylacetylene[a,b].

T (°C)	50	60	70	80	90
Yield (%)	24	31	52	92	93

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), Ag NPs (10.0 mg), water (1.0 mL), 8 h.
[b] Isolated yield.

Table 2
Optimization of catalyst amount for reaction of benzylazide with phenylacetylene[a,b].

Entry	Amount of catalyst/g	Time/h	Yield/%
1	–	12	0
2	0.0010	12	26
3	0.0050	12	68
4	0.0100	8	92
5	0.0150	8	93

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), water (1.0 mL), 80 °C.
[b] Isolated yield.

Fig. 4. TGA of blank resin and Ag NPs.

Table 3
Substrate scope of reaction between various azides and alkynes.[a]

Entry	R–N₃	Alkyne	Time/h	Product	Yield/%[b]
1	1a	2a	8	3a	95
2	1a	2b	7	3b	95
3	1a	2c	8	3c	96
4	1a	2d	15	3d	93
5	1a	2e	9	3e	94
6	1a	2f	8	3f	94
7	1b	2a	8	3g	95
8	1d	2a	8	3h	96
9	1e	2a	8	3i	92
10	1e	2c	8	3j	93

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), Ag NPs (10 mg), water (1.0 mL), 80 °C.
[b] Isolated yield.
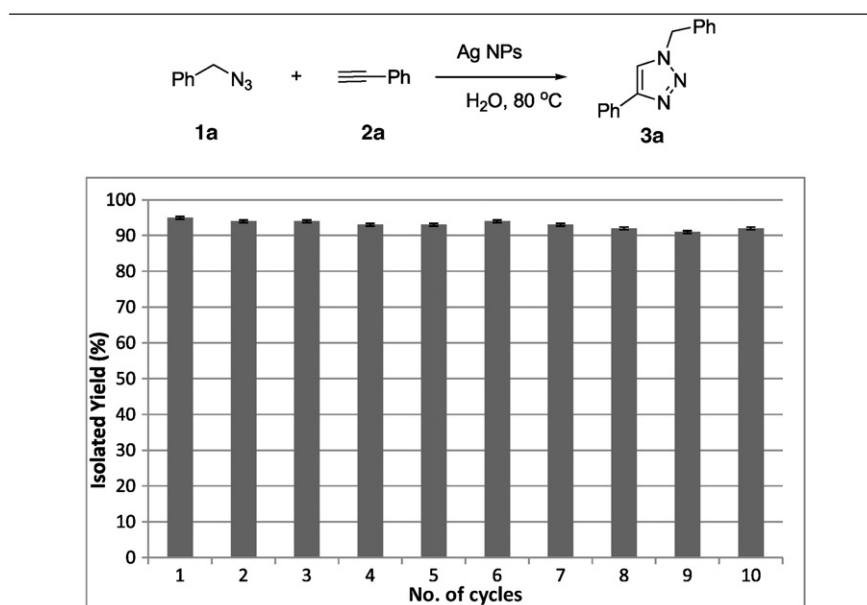
Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), water (1.0 mL), Ag NPs (10 mg), water (1.0 mL), 80°C.

Fig. 5. Recycling of catalyst Ag NPs in aqueous reaction of benzylazide with phenylacetylene.

8 h. The higher temperature did not accelerate the reaction time or promote the reaction yield (Table 1).

The amount of catalyst was investigated. The results are summarized in Table 2. Product **3a** was formed in high yields with catalyst loadings of 0.010 g (the catalyst includes of resin and Ag NPs). The reaction was not carried out without catalyst. A higher amount of catalyst did not accelerate the reaction time or promote the reaction yield much more than catalyst loadings of 0.010 g. A lower yield of product **3a** was obtained with a lower amount of catalyst and in a reaction time of 12 h.

Using optimal reaction conditions, various alkynes were reacted with azides in the presence of Ag NP$_S$ in water (Table 3). Phenyl-acetylene and electron-rich aromatic alkynes gave excellent results with benzyl azide. However, an electron-deficient aromatic alkyne needs a longer time to form the 1,2,3-triazole product under the same reaction conditions. The reaction also gave an excellent yield when the reaction time was extended to 15 h. Aliphatic alkynes required longer reaction times to give high yields compared with electron-rich aromatic alkynes, but the reactions were completed within 10 h.

We examined the recyclability of the nanosilver catalyst (Fig. 5). Product **3a** was dissolved in dichloromethane and the catalyst nano-silver was filtered from the reaction mixture and used directly for another cycle. As shown in Fig. 5, the catalyst showed no substantial reduction in activity even after the tenth run. All reactions were completed in 8 h and afforded **3a** in yields of 90–95%.

In conclusion, Ag NPs embedded in polyallylamine resin were used as a novel and efficient catalyst for the azide–alkyne click reaction in water. Attractive features of this procedure include its green reaction conditions, medium reaction times, excellent yields and operational simplicity. The catalysts can be recycled more than ten times without an obvious loss in catalytic activity. We believe that this simple and green procedure is a practical method for use in academia and chemical industries. The scope and synthetic application of the nanosilver are under investigation.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2015.11.005.

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